

Non-adiabatic effects of superconductor silane under high pressure

Fan Wei^{1,*}, Wang Jiang-Long^{2,1}, Zou Liang-Jian¹, and Zeng Zhi¹

¹*Key Laboratory of Materials Physics, Institute of Solid State Physics, Hefei Institutes of Physical Sciences, Chinese Academy of Sciences, 230031-Hefei, People's Republic of China*

²*Department of Physics, Hebei University, 071002-Baoding, People's Republic of China*
(Dated: August 18, 2010)

Investigations of non-adiabatic effects by including vertex corrections in the standard Eliashberg theory show that high phonon frequency is unfavorable to superconductivity in regime of strong vertex correction. This means that it is hard to find high-transition-temperature superconductors in the compounds with light elements if the non-adiabatic effects are strong. The interplay interaction between non-adiabatic effect and Coulomb interaction makes the transition temperature of silane superconductor not so high as predicted by the standard Eliashberg theory.

PACS numbers: 74.20.Fg, 74.62.Fj, 74.70.Ad

The recently found superconductor silane (SiH_4) at high-pressure [1] partially realizes the theoretical predictions of high-temperature superconductors of hydrogen dominant metallic alloy [2] and metallic hydrogen at high pressure [3]. However, the transition temperature (T_c) is significantly lower than the values predicted in previously theoretical calculations [4–7]. What is the underlying mechanism of the lower T_c compared with the higher T_c predicted in strong-coupling theory. With increasing pressure the electronic structures of silane will evolve from molecule-like energy-levels to electron-bands when gaseous silane transforms into crystalline silane. The effective band-widths of conducting electrons of metallic silane are narrow so that the non-adiabatic effects will be prominent. It's very desirable study the influences of non-adiabatic effects on T_c .

The non-adiabatic effects are partially included in the vertex corrections in the theory of electron-phonon interaction. The Eliashberg theory [8–10] combined with the vertex corrections had been widely studied by perturbation method [11–13]. We have performed a full parameter-space search based on Eliashberg theory with and without vertex corrections [13, 14]. In this paper, we study the influences of the vertex corrections on T_c of superconductor silane at high pressure using reliable Eliashberg functions $\alpha^2 F(\omega)$ obtained from the calculations of linear-response theory [4]. Our results indicate that the vertex correction can efficiently suppress T_c approaching to the values found in experiments. Additionally, we find that high phonon frequency is unfavorable to high- T_c if the strong vertex corrections are included. This means that it is hard to realize high- T_c superconductors in silane and other hydrogen-rich materials.

We have generalized the equation of energy gap in Ref.[11] by including the Coulomb interaction [13]. The calculations of vertex corrections are greatly simplified under isotropic approximation. The electron-phonon interactions are included in the vertex corrections only by

the functions λ_n defined as $\lambda_n = 2 \int_0^\infty d\nu \alpha^2 F(\nu) \nu / (\nu^2 + \omega_n^2)$. When temperature is very close to T_c , the energy-gap equation including the leading vertex correction from electron-phonon interaction is written as $\sum_{n'=-\infty}^{+\infty} K_{nn'} \Delta_{n'} / |\omega_{n'}| = 0$ with the kernel matrix

$$K_{nn'} = [\lambda_{n-n'} B_{nn'} - \mu^* + C_{nn'}] a_{n'} - \delta_{nn'} H_{n'} \quad (1)$$

where the definitions of H_n , $A_{nn'}$, $B_{nn'}$, $C_{nn'}$ and a_n are presented in Ref.[11, 13]. In order to calculate T_c , the matrix $K_{nn'}$ is symmetrized with the same manner as in Ref.[10]. The E_B is the effective band-width and the Coulomb pseudo-potential μ^* is defined as $\mu^* = \mu_0 / (1 + \mu_0 \ln(E_B/\Omega_0))$, where $\mu_0 = N(0)U$, $N(0)$ the density of state at Fermi energy E_F , U the Coulomb interaction between electrons and Ω_0 characteristic energy of typical phonon correlated to superconductivity. Generally, the ratio Ω_0/E_B takes as the parameter to measure vertex correction and the larger Ω_0/E_B is corresponding to the stronger vertex correction. In this context, the vertex corrections are controlled by E_B , the smaller E_B (or larger Ω_0/E_B) for stronger vertex corrections. With development of method of electronic-structure calculation in solid materials, the parameters of electron-phonon interaction can be calculated using density functional theory combined with perturbing linear-response theory [15, 16]. The Eliashberg functions $\alpha^2 F(\omega)$ obtained by linear response theory are easily merged in the formulae used in this context.

In the standard Eliashberg theory, T_c will infinitely increase with phonon frequency or energy. It's widely expected that high-temperature superconductors should be found in compounds containing light elements such as hydrogen-rich material silane and metal hydrogen at high pressure. We will see that the non-adiabatic effects set bounds to infinitely increasing T_c . In order to obtain very general results, at first step, we apply the simple phonon spectrum and Eliashberg function $\alpha^2 F(\omega)$ used in Ref.[9]. The Fig.1 shows how T_c changes with Ω_P and E_B . We can see that for large band-width $E_B=5$ eV (weak vertex correction), T_c increases monotonously with Ω_P just as in the standard Eliashberg theory. However for very strong vertex correction with small band-width $E_B=1$ eV, T_c is

*Electronic address: fan@theory.issp.ac.cn

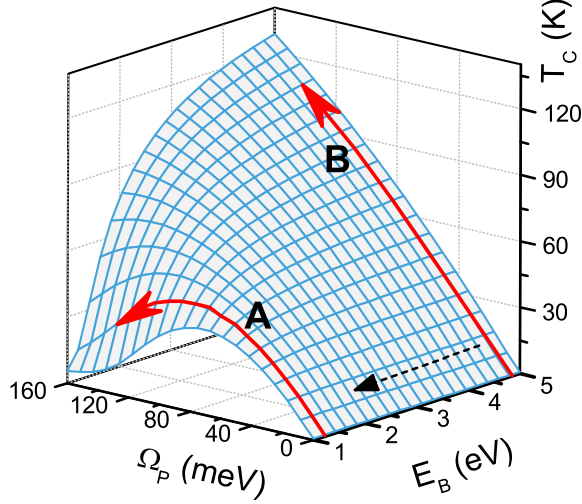


FIG. 1: The T_c on $\Omega_P - E_B$ parameter plane. The two solid arrows **A** and **B** show the changes of T_c with Ω_P at fixed E_B (**A**) near 1 eV and (**B**) 5 eV respectively. The dashed arrow shows the direction enhanced the vertex corrections.

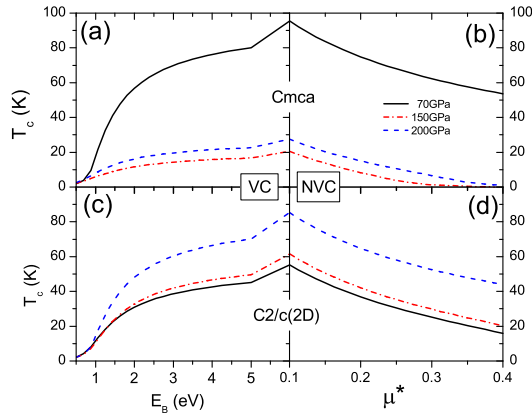


FIG. 2: The dependence of T_c on E_B and μ^* , based on the Eliashberg functions $\alpha^2 F(\omega)$ obtained from linear-response theory at different pressures for the *Cmca* structure (a,b) and *C2/c(2D)* structure (c,d) respectively [4]. The (a) and (c) include vertex corrections (VC), and there are no vertex corrections (NVC) in (b) and (d).

non-monotonously dependent on Ω_P . When Ω_P is larger than a threshold value, T_c will decrease with Ω_P . This means that, if the vertex corrections are included, high phonon energy is unfavorable to superconductivity.

We preform the calculations of the vertex corrections of real superconducting material silane containing the lightest element: hydrogen. The lowest order vertex correction can significantly reduce T_c when energy of phonon Ω_P is larger than 80 meV shown in Fig.1. We adopt the Eliashberg functions that had been reported

in Ref [4] in the calculations of linear-response theory. The structures of crystal silane at high-pressures haven't been completely defined. The metallic *P6₃* structure had been found in experiment [1]. The theoretical layered structure with *Cmca* space-group symmetry is more stable from 60-200 GPa [4], other stable structures at higher pressures had been already reported [17]. The hydrogen-rich superconductor silane at higher pressure has very high phonon energies coming from the vibrations of hydrogen atoms. The effective phonon energies $\langle \omega \rangle_{ln}$ for silane at high pressures distribute from 50 meV to 75 meV dependent on pressures. The parameters λ of electron-phonon interaction are about 1.17, 0.62, 0.75 for the *Cmca* structure and 0.84, 0.87, 1.1 for the *C2/c(2D)* structure respectively when pressure increases from 70 GPa to 150 GPa and to 200 GPa. The T_c calculated using Allen-McMillan formula are distributed from 20 K to 80 K [4] that are greatly larger than experimental $T_c < 17$ K.

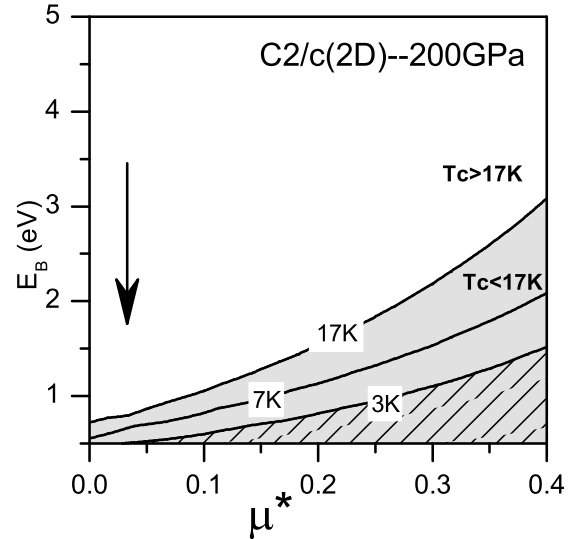


FIG. 3: The T_c on $\mu^* - E_B$ plane using the Eliashberg functions $\alpha^2 F(\omega)$ obtained from linear-response theory [4]. The structure has *C2/c(2D)* space group symmetry at pressure 200 GPa. The shade areas are regions with $T_c < 17$ K. The arrow shows the directions of increasing the vertex correction.

As reported in Ref.[4], the pressure-dependence T_c of the *Cmca* structure is different from the *C2/c(2D)* structure. The T_c of the *Cmca* structure decreases when pressure increases from 70 GPa to 150 GPa, and slightly increases with increasing pressure further to 200 GPa. However for the *C2/c(2D)* structure, T_c monotonously increases with pressures from 70 GPa to 200 GPa. We first present the results of the *Cmca* structure in detail shown in Fig.2(a,b). If the vertex corrections are not included and $\mu^* = 0.1$, the values of T_c are close to 20 K at pressures 150 GPa and 200 GPa, which are smaller than those obtained from McMillan formula. So our results indicate that for very broad distributed phonon

spectrum, the standard strong-coupling calculations are needed to accurately calculate T_c beyond simple McMillan and Allen T_c formulae.

At low pressure with larger inter-molecule distances, the crystalline silane is an insulator with narrow energy bands corresponding to discrete energy levels of a single molecule. The effective band-widths will increase with increasing pressures and overlaps of molecular orbits of different molecules. If the vertex corrections are included in our calculations with the effective band-width E_B of conducting electrons from 0.5 eV to 5 eV, the T_c at 150 GPa and 200 GPa are significantly reduced to the value smaller than 17 K shown in Fig.2(a). The effective band-widths obtained from the density functional calculations increase from very small values at low pressure to about 1.0-3.0 eV at 100-200 GPa for the $C2/c(2D)$ and $Cmca$ structures [4]. In another case, the effects of Coulomb interaction are more significant because the T_c decreases to very small values with increasing μ^* at 150 GPa and 200 GPa shown in Fig.2(b). If we want to know what is more important for the depression of T_c we should know real value of μ^* at 150 GPa and 200 GPa. At 70 GPa, the small band-widths with $E_B < 1$ eV guarantee the T_c lower than 17 K. We find that, if without vertex correction, even larger μ^* ($=0.4$) can not suppress T_c to value smaller than 17 K at 70 GPa.

The effects of vertex correction of the $C2/c(2D)$ structure in Fig.2(c) are similar to the $Cmca$ structure in Fig.2(a), however the influences of the Coulomb interaction in Fig.2(d) are different from the $Cmca$ in Fig.2(b). The $C2/c(2D)$ structure is less stable than the $Cmca$ structure. The stronger electron-phonon interaction induces its structure more unstable at high pressures from 150 GPa to 200 GPa. Theoretical values of T_c increase with pressures. This is because the enhancements of T_c induced by the increase of λ are larger than the depressions of T_c due to the vertex correction. For the $C2/c(2D)$

structure, the Coulomb interaction depresses T_c to values which are still larger than 17 K shown in Fig.2(b). So Coulomb interaction individually can not explain why T_c smaller than 17 K in high-pressure experiments. The effective band-widths E_B of conducting electrons in the $C2/c(2D)$ structure are larger than 1 eV at 150 GPa and 200 GPa [4] so that the vertex correction individually can not explain low T_c at 100 GPa and 200 GPa as well as shown in Fig.2(c). The Fig.3 illustrates the T_c for the $C2/c(2D)$ structure on μ^*-E_B plane at pressure 200 GPa. The shading region in the figure shows the effective region with parameters μ^* and E_B that can explain the T_c smaller than 17 K, which is only small area of parameter-space with $\mu^* > 0.1$ and $E_B < 2.0$ eV. Especially, the hatched region shows the parameter-space to explain why experimental T_c is smaller 3 K at 200 GPa. So our results indicate that the interplay of vertex correction and Coulomb interaction can explain the low T_c of the $C2/c(2D)$ structure. Our calculations can not fully explain pressure-dependent T_c in Ref [1], especially, the higher $T_c=17$ K near 100-120 GPa because of the lack of information of structural changes.

In summary, we study the effects of the vertex correction on T_c for superconductor of silane at high pressure. Our results indicate that the non-adiabatic effects are the barrier to prevent T_c from increasing infinitely with phonon frequency. This means that it is hard to realize high T_c to home temperature in high pressure rich-hydrogen materials. Our results also show that the interplay interaction between Coulomb interaction and vertex correction is essentially to explain the larger differences between theory and experiments.

The author (Fan W) thanks Dr. Li Yan-Ling for the helpful discussions. The work preforms in the Center for Computational Science of CASHIPS and is supported by Knowledge Innovation Project of Chinese Academy of Science.

-
- [1] Eremets M I, Medvedev I A, Tse J S and Yao Y 2008 Science **319** 1506
 - [2] Ashcroft N W 2004 Phys. Rev. Lett. **92** 187002
 - [3] Ashcroft N W 1968 Phys. Rev. Lett. **21** 1748
 - [4] Chen X J, Wang J L, Struzhkin V V, Mao H K, Hemley R J and Lin H Q 2008 Phys. Rev. Lett. **101** 077002 and supplemental materials
 - [5] Feng J, Grochala W, Jaroń T, Hoffmann R, Bergara A and Ashcroft N W 2006 Phys. Rev. Lett. **96** 017006
 - [6] Pickard C J and Needs R J 2006 Phys. Rev. Lett. **97** 045504
 - [7] Yao Y, Tse J S, Ma Y and Tanaka K 2007 Eur. Phys. Lett. **78** 37003
 - [8] Éliashberg G M 1960 Soviet. Phys. JETP, **11** 696
 - [9] Scalapino D J, Schrieffer J R and Wilkins J W 1966 Phys. Rev. **148** 263
 - [10] Allen P B and Dynes R C 1975 Phys. Rev. **B 12** 905
 - [11] Kostur V N and Mitrović B 1994 Phys. Rev. **B 50** 12774
 - [12] Grimaldi C, Pietronero L and Strässler S 1995 Phys. Rev. **B 52** 10530
 - [13] Fan W 2009 Physica C **469** 177
 - [14] Fan W 2008 Chinese Phys. Lett. **25** 2217
 - [15] Savrasov S Y and Savrasov D Y 1996 Physical Review **B 54** 16487
 - [16] Baroni S, de Gironcoli S, Dal Corso A and Giannozzi P 2001 Rev. Mod. Phys. **73** 515
 - [17] Martinez-Canales M, Oganov A R, Ma Y M, Yan Y, Lyakhov A O and Bergara A 2009 Phys. Rev. Lett. **102** 087005